

was extracted with 750 cc. of boiling water and the insoluble material removed by filtration. The aqueous solution was evaporated to dryness whereby 15 g. (40%) of crude trihydrate of sulfodehydroabiatic acid was obtained m. p. 221° (cor.) decompn.

For further identification the sulfonate was converted into the dimethyl ester: m. p. 177–177.5° (cor.), which did not lower the melting point in the mixed melting point test with authentic material.<sup>4b</sup>

*Anal.* Calcd. for  $C_{22}H_{32}O_5S$ : C, 64.69; H, 7.86. Found: C, 65.05; H, 7.78.<sup>10</sup>

The insoluble material obtained from the water extraction of the sulfonation product was dissolved in ether and the ether extracted with two portions of 100 cc. of a 3% sodium hydroxide solution and then with water. After drying the ether solution with anhydrous sodium sulfate and evaporating the ether, 5 g. of a solidifying residue was obtained which yielded 1.5 g. (20%) of lactone of hydroxy-tetrahydroabiatic acid which, when recrystallized from acetone, melted at 131.5–132° (cor.). This material did not produce any lowering of melting point with a sample of the authentic compound.<sup>11</sup>

*Anal.* Calcd. for  $C_{20}H_{32}O_2$ : C, 78.88; H, 10.60. Found: C, 78.78; H, 10.48.

The sodium hydroxide solution containing the acidic material from the preparation of the lactone was made acid with hydrochloric acid and yielded 10 g. of a hard resin which was not investigated further.

**The Preparation of Dehydro- and Dihydroabiatic Acid from Rosin.**<sup>12</sup>—Ordinary N-wood rosin was subjected to the same treatment as above, but using varying amounts of iodine as a catalyst. This treated rosin, when subjected to sulfonation, yielded the trihydrate of sulfodehydroabiatic acid and lactone of tetrahydroabiatic acid isolated in the following amounts:

Catalyst, %	Apparent softening point, °C.	( $\alpha$ ) <sub>D</sub> <sup>20</sup> (1% ethanol solution)	Acid number	Sulfonic acid, %	Lactone, %
(1) 0.0	76.0	− 7.4°	162.3	4.0	4.2
(2) .1	75.5	−19.5°	162.9	3.5	3.4
(3) .2	76.5	−10.0°	163.4	9.5	2.0
(4) .5	74.5	− 8.1°	162.7	11.0	3.0
(5) 1.0	73.0	− 3.5°	160.8	16.0	4.0
(6) 1.5	70.5	+16.5°	158.1	41.0	4.6
(7) 2.0	69.0	+25.8°	155.2	48.0	4.7

The trihydrate of the sulfonate of dehydroabiatic acid was recrystallized from water and was obtained pure after two crystallizations from this solvent, melting at 223–224° (cor.) decompn.<sup>13</sup>

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(10) All analyses by Mr. S. Gottlieb, Columbia University, New York City, New York.

(11) Hasselstrom, Brennan and McPherson, *THIS JOURNAL*, **60**, 1267 (1938).

(12) Subject matter for U. S. Patent Application.

(13) Crude talloel from sulfate pulp black liquor may be subjected to the same treatment whereby the isolated resin acids show the following characteristics: m. p. 173–175° (cor.); [ $\alpha$ ] +54.1° (1 g. in 100 cc. of ethanol), giving high yields of the trihydrate of sulfonate of dehydroabiatic acid on sulfonation. Subject matter for U. S. Patent Application.

## Depression of the Melting Point of $\alpha$ -Toxicarol and Related Compounds in Soft-glass Capillary Tubes\*

BY HOWARD A. JONES AND JOHN W. WOOD

Values obtained by different investigators for the melting point of  $\alpha$ -toxicarol have shown considerable variance. Cahn, Phipers and Boam<sup>1</sup> state that the presence of varying amounts of  $\beta$ -toxicarol in most samples of  $\alpha$ -toxicarol largely accounts for this. These workers report 232–233° for the melting point of pure  $\alpha$ -toxicarol, but others have not been able to prepare samples with this value.

The writers have now found that the type of glass from which the capillary tubes are made has a marked effect on the melting point of this substance. Lower values were observed in soft-glass tubes. In Table I are shown the melting points of various samples of  $\alpha$ -toxicarol and  $\beta$ -toxicarol, rotenone, deguelin, and anthracene (used as a check) in different types of glass and in silica tubes. Preliminary results in cleaned and uncleaned tubes were not significantly different, contrary to the experience of Schoorl<sup>2</sup> and of George<sup>3</sup> with certain alkali-sensitive substances. Nevertheless all tubing was allowed to remain overnight in sulfuric acid dichromate solution, rinsed thoroughly with distilled water, let stand at least three days in distilled water with several changes of water a day, and then dried, drawn to capillary size and used within two or three days. In one case soft glass capillaries were cleaned in this same way after drawing and the melting point of  $\alpha$ -toxicarol in these was not significantly different from that in tubes drawn from cleaned soft glass. To obtain a rough indication of the relative alkalinity of the glasses and the silica used the pH of a suspension of 5 g. of the powdered (60 mesh) material in 5 cc. water (pH 5.9) was determined with a Beckman pH meter (glass electrode) fifteen to twenty minutes after the addition of the water. Melting points were determined in a modified Markley melting-point apparatus<sup>4</sup> by means of a carefully standardized thermometer. In addition, some determinations were made by the microscope hot stage method with the sample resting on soft-glass slides.

\* Not subject to copyright.

(1) Cahn, Phipers and Boam, *J. Chem. Soc.*, 513 (1938).

(2) Schoorl, *Z. physik. Chem.*, **A160**, 158 (1932).

(3) George, *Helv. Chim. Acta*, **15**, 924 (1932).

(4) Schechter and Haller, *Ind. Eng. Chem., Anal. Ed.*, **10**, 392 (1938).

TABLE I  
MELTING POINTS (°C., COR.) OF  $\alpha$ - AND  $\beta$ -TOXICAROL, ROTENONE, DEGUELIN, AND ANTHRACENE IN CAPILLARY TUBES AND BY MICROSCOPE HOT-STAGE

Method	pH of suspension, 5 g./5 cc.	$\alpha$ -Toxicarol				$\beta$ -Toxicarol		Rotenone	Deguelin	Anthracene
		1	2	3 <sup>a</sup>	Samples 4 <sup>a</sup>	1	2 <sup>a</sup>			
In capillary tubes:										
Pyrex glass (no. 774)	9.0	230-231	228-229	229.5-230.5	223-225	180-182	165-167°	163-164	169-170	214-215
Ordinary soft glass	10.0	205-206	210-212	207.5-209.5	214.5-218	176-178	164.5-165.5°	159.5-160.5	163.5-164.5	214-215
Tamworth Glasbake glass	9.0	230-231	.....	230-231	.....	.....	.....	.....	.....	214-215
Kimble glass	10.2	205-206	.....	207.5-209	.....	.....	.....	.....	.....	.....
Corning alkali resistant glass (no. 728)	10.2	207-207.5	.....	208-209.5	.....	.....	.....	.....	.....	.....
Corning electrode glass (no. 015)	11.0	200-201	.....	201-203	.....	.....	.....	155-156	.....	214-215
Transparent silica	6.2	230.5-231	.....	230-231	.....	.....	.....	163.5-164	.....	.....
By microscope hot stage <sup>b</sup>		226-228	.....	227-231	.....	179-182	163°	164	.....	.....

<sup>a</sup> These samples were kindly furnished by R. S. Cahn. <sup>b</sup> These values were determined by William A. Stanton of the University of Maryland. <sup>c</sup> Partial melting, see text.

Samples of  $\alpha$ -toxicarol were prepared by alkali treatment of extracts of derris root and recrystallization of the separated crude material from benzene. According to the Goodhue<sup>5</sup> color test and the results of Cahn, Phipers and Boam,<sup>1</sup> sample 1 contained 1.7% and sample 2 contained 2.3% of  $\beta$ -toxicarol. Samples 3 and 4 were kindly furnished by R. S. Cahn, of the Cooper Technical Bureau, London, and were stated to have melting points of 229-230° and 225-227°, with 2.3% and 4.5% of  $\beta$ -toxicarol, respectively. A sample of  $\beta$ -toxicarol was prepared by the method of Cahn and co-workers,<sup>1</sup> which, according to the Goodhue color test, was about 95% pure. Another sample, obtained from Dr. Cahn, was said to be pure and to have a melting point of 164-165°. Samples of rotenone and deguelin were prepared in the usual way.

It will be noted that the melting points of  $\alpha$ -toxicarol in all the soft glasses are markedly lower than in Pyrex and Tamworth glass and silica, although all samples did not show the same difference between the hard and soft glasses. Sample 4, which is less pure both by the criterion of a lower melting point and by lack of sharpness of melting, does not give so low a value in soft glass as do other apparently purer samples, although the value ranged over several degrees. From samples 1 and 3 it will be seen that the glasses in which lower values were obtained were the more alkaline and that the glass in which the lowest values were obtained was the most alkaline. In fact, in this glass (Corning electrode) marked differences were obtained depending on the rate of heating. If the rate of heating at 10-15° below the melting point was much slower than the usual 1° per minute, values of 196-198° were obtained for samples 1 and 3. When some of sample 1 was mixed with a small proportion of powdered ordinary soft glass, the melting point, determined in a Pyrex tube, was about 196°. Another sample of this material similarly mixed with powdered Corning electrode glass melted at about 192° in Pyrex with some browning of the material before melting. The same mixture in tubes of Corning electrode glass melted at about 190° when heated at the usual rate and at about 185° when heated very slowly; in both cases the melting point was very unsharp, with considerable

browning before melting. The alkalinity of the glass appears to be the principal factor causing the observed lowering of melting points. According to Cahn, Phipers and Boam<sup>1</sup> the presence of alkali sets up a reversible equilibrium between  $\alpha$ - and  $\beta$ -toxicarol. It is quite likely that this is the reaction induced in the soft glasses, with a resultant lowering depending upon the alkalinity of the glass, the area of contact surface, the original purity of the sample, and other factors. Apparently Pyrex and Tamworth glasses are not sufficiently alkaline to induce this change, since values in them are in agreement with those in silica.

The effect of the glass is definite but much less marked with  $\beta$ -toxicarol than in the case of  $\alpha$ -toxicarol. The value obtained for sample 1 is higher than that reported by Cahn and co-workers<sup>1</sup> for this compound. At the temperature indicated this sample melted to a cloudy liquid and under the microscope showed a small amount of crystals in a liquid melt. These crystals disappeared (melted or dissolved) at 193.5°. The sample obtained from Dr. Cahn definitely began to melt at the temperature stated, but some semisolid material remained on the side and bottom of the tube. On several trials the bath was allowed to cool below 150° and then reheated. No change was observed between 165 and 170°, as the temperature rose a very gradual melting and clearing was observed, and usually between 177 and 184° all the material appeared to have melted to a cloudy liquid. Under the microscope this sample began to melt at about 163°. Its behavior above this point was similar to that observed in a capillary. At roughly 177° it appeared to be mostly liquid, with a few crystals present. These crystals finally disappeared at 191°. In this last respect the sample behaved similarly to that prepared in this Laboratory. Further investigation is necessary in order to determine whether the behavior of  $\beta$ -toxicarol is caused by varying proportions of  $\alpha$ -toxicarol or by dimorphism.

Rotenone and deguelin show small but definite differences in melting point in Pyrex and in soft glasses, but anthracene exhibits the same value in hard as in soft glasses.

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(5) Goodhue, *J. Assoc. Off. Agr. Chem.*, **19**, 118 (1936).